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3,471,431

TERMINAL SULFONATE POLYMERS, LATICES
THEREOF, AND METHOD OF PREPARATION

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No Drawing. Filed Mar. 4, 1966, Ser. No. 533,805
Int. Cl. C08d 5/00

U.S. Cl. 260—29.7

10 Claims

ABSTRACT OF THE DISCLOSURE

A process for preparing a monosulfonated polymer by dissolving a polymer having a single terminal alkali metal radical and reacting therewith a sultone. The disclosure also covers the monosulfonated polymer as well as latices made from mixtures of monosulfonated and unsulfonated polymers.

This invention relates to novel terminally sulfonated polymers, their preparation and latices made therefrom.

The preparation of polar substituted derivatives of polymeric materials has been studied in many aspects; however, the production of polymers having a polar group placed in a specifically designated position is rare. In one of the few types of polymerization in which specific position designation of polar substitution can be made, the polar radicals are placed on both ends of a polymer chain. In many cases this results in gelation of the polymer, either due to its association characteristics or due to cross-linking which can readily occur.

Recently developed polymers which are of special interest are block copolymers of monovinyl arenes with conjugated diolefins made in such a way as to produce "self-curing" block copolymers of the general configuration.

A—B—A

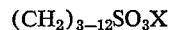
wherein each A is a polymer block of a monovinyl arene and B is a polymer block of a conjugated diene, as well as hydrogenated products thereof. These materials have been found to be extremely useful because they do not require vulcanization especially when the desired relationship of molecular weight between the several blocks is present. However, they possess one disadvantageous property which it would be highly desirable to correct or overcome, namely, that they produce relatively unstable latices. The reason for this is obscure, but microscopic examination of some latices shows a number of irregularly shaped particles present in the form of disc or saucer shapes, contrasted to the desirable spherical shape which is characteristic of stable latices.

Other problems which have not been solved satisfactorily comprise the production of latices of what may be termed high impact polystyrene wherein the styrene latex is modified by the presence of an elastomeric component, since in many instances the addition of one or the other of these components results in an unstable latex which readily coagulates. Furthermore, it is often desirable to improve the processability or green strength properties of certain rubbers contained in latex form but the addition of a block copolymer in the form of a latex often destabilizes the latex and results in massive coagulation.

It is an object of the present invention to provide an improved process for the production of sulfonated polymers. It is another object of the invention to provide improved monosulfonated terminally substituted polymers. It is a special object of the invention to provide improved polymeric latices. Other objects will become apparent during the following detailed description of the invention.

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Now, in accordance with the present invention, novel sulfonated polymers are provided wherein only one terminal of each polymer chain bears a sulfonate radical. More particularly, the sulfonate radical has the general configuration



wherein X is a radical of the group consisting of hydrogen, alkali metal or ammonium ions. The polymers of which each linear chain is terminated on one end only with the subject sulfonate radicals comprise homopolymers of conjugated dienes, homopolymers of monovinyl arenes, random copolymers of monovinyl arenes with conjugated dienes and block copolymers of monovinyl arenes with conjugated dienes.

Still in accordance with the present invention, novel latices having excellent mechanical stability comprise a continuous aqueous phase and as a discontinuous phase at least one of the monosulfonated polymers. In further accordance with the invention, modified latices comprise those just described containing in addition a non-sulfonated polymer of the group consisting of elastomeric conjugated diene homopolymers, monovinyl arene homopolymers, random copolymers of monovinyl arenes with conjugated dienes and block copolymers of monovinyl arenes with conjugated dienes, the weight ratio of sulfonated polymer to unsulfonated polymer being between 1:1 and 10:1.

Another aspect of the present invention comprises the process for the formation of the subject sulfonated polymers which comprises forming a solution of a "living" polymer wherein each chain is terminated on one end only with an alkali metal radical and reacting therewith an aliphatic sultone, said sultone, having from 3 to 12 carbon atoms per molecule.

The novel products of the invention broadly comprise the subject class of polymers and copolymers which are essentially linear polymeric molecules, one terminal of each polymer chain bearing a sulfonate radical. These are to be distinguished from polymers in which both terminals of the polymer chains are sulfonated since it has been found that the latter type of products leads rapidly to gelation and cross linking which reduce their utility and ease of processing. Moreover, the type of polymers in which both terminals are sulfonated do not form satisfactory latices due to the high polarity of the molecules and consequent tendency thereof to create stable foams rather than true latices.

The polymers which may be monosulfonated according to the present invention include homopolymers of conjugated dienes such as polystyrene or polybutadiene; homopolymers of monovinyl arenes such as polystyrene or polyalpha-methyl styrene; random copolymers of monovinyl arenes with conjugated dienes such as styrene-butadiene copolymers having either elastomeric or thermoplastic properties dependent upon the ratio of the two monomers; and especially block copolymers of monovinyl arenes with conjugated dienes. In the latter class, block copolymers are especially contemplated having either two or three block components. Typical of these are the two-block copolymers having the typical structure polystyrene-polybutadiene and three-block copolymers such as those having the structure polystyrene-polybutadiene-polystyrene or polystyrene-polyisoprene-polystyrene. These polymers may be subjected to hydrogenation, if desired, to reduce the original unsaturation. While double bonds in either or both the vinyl arene or conjugated diene portions of the polymer may be reduced, it is preferred to reduce the unsaturation of at least the diene portion by at least about 50%.

It is especially contemplated that these block copolymers be elastomeric but if the monovinyl arene content